Review

Biofpr
Biofuels Bioproducts & Biorefining

Feedstock handling and processing effects on biochemical conversion to biofuels

Daniel Inman and Nick Nagle, National Renewable Energy Laboratory, Golden, CO, USA
Jacob Jacobson, Erin Searcy and Allison E. Ray, Idaho National Laboratory, Idaho Falls, ID, USA

Received March 25, 2010; revised July 6, 2010; accepted July 8, 2010
View online at Wiley Online Library (wileyonlinelibrary.com); DOI: 10.1002/bbb.241;
***Biofuels, Bioprod. Bioref.* 4:562–573 (2010)**

Abstract: Abating the dependence of the United States on foreign oil by reducing oil consumption and increasing biofuels usage will have far-reaching global effects. These include reduced greenhouse gas emissions and an increased demand for biofuel feedstocks. To support this increased demand, cellulosic feedstock production and conversion to biofuels (e.g. ethanol, butanol) is being aggressively researched. Thus far, research has primarily focused on optimizing feedstock production and ethanol conversion, with less attention given to the feedstock supply chain required to meet cost, quality, and quantity goals. This supply chain comprises a series of unit operations from feedstock harvest to feeding the conversion process. Our objectives in this review are (i) to summarize the peer-reviewed literature on harvest-to-reactor throat variables affecting feedstock composition and conversion to ethanol; (ii) to identify knowledge gaps; and (iii) to recommend future steps. © 2010 Society of Chemical Industry and John Wiley & Sons, Ltd

Keywords: biochemical conversion; pre-processing; biomass composition; feedstock logistics

Introduction

Global extraction of oil is expected to peak in the near future, if it hasn't already.[1] Dwindling oil supplies, coupled with concerns over the impact of increasing atmospheric CO_2 levels from the combustion of fossil fuels,[2] have led many countries to adopt aggressive programs to rapidly develop and deploy renewable sources of energy. Because of the dependence of the transportation sector on petroleum-based liquid fuels, much of this effort has focused on developing alternative liquid transportation fuels. In the USA, significant research attention has been directed toward bioethanol derived from both first- and second-generation feedstocks (starch and lignocellulosic biomass, respectively), with ethanol derived from the former being produced at an industrial scale both in the USA and throughout the world.

Correspondence to: Daniel Inman, National Bioenergy Center, National Renewable Energy Laboratory, 1617 Cole Blvd., Golden, CO 80401-3393, USA.
E-mail: Daniel.Inman@nrel.gov

Globally, ethanol production has increased dramatically over the last five years. In 2008, worldwide ethanol production exceeded 64 billion liters, 53% and 38% of which was produced in the USA (using corn grain as the main feedstock) and Brazil (using sugarcane as the main feedstock), respectively.[3]

In addition to being the world's largest producer of ethanol, the USA is the world's top consumer of crude oil and the second largest greenhouse gas (GHG) emitter, behind China. An average of 20 680 000 barrels (3 287 857 m^3) of oil per day were consumed in the USA in 2007, which amounts to approximately 24% of the 2007 worldwide oil consumption.[4] Burning fossil fuels to accommodate transportation is responsible for the emission of roughly 5720 Tg CO_2-equivalents annually.[5,6] Because the USA is responsible for a disproportionate amount of global oil consumption and GHG emissions, significant improvements in renewable fuels use by the US transportation sector will have far-reaching global implications on petroleum availability and atmospheric CO_2 level increases.

Progressive legislation to help curb oil consumption and GHG emissions is beginning to take hold in the USA at both the state and federal levels.[7,8] For example, the 2007 Renewable Fuel Standard (RFS), which is mandated in the Energy Independence and Security Act of 2007 (EISA), is intended to spur the growth of advanced and cellulosic biofuels industries by promoting research in these areas and mandating aggressive market penetration targets. These targets culminate in the year 2022 with a minimum annual production volume of 36 billion gallons per year (bgy) of renewable fuel, of which 16 bgy are targeted to be derived from cellulosic materials, 4 bgy are envisaged to be 'advanced biofuel', and 1 bgy will be biomass-based diesel.[8] Though not explicit in the bill, the remaining 15 bgy of renewable fuel will most likely come from corn-grain-based ethanol because the industry is well established and is on track to easily meet, if not exceed, this production volume within a few years.

Although the increasing use of renewable transportation fuels is promising, commercial production of these fuels is fraught with serious logistical issues; top among them is sustainable feedstock availability and economic feedstock supply. Assuming that the RFS goals will be met with ethanol, it is estimated that the nation's biorefineries will need 700 million metric tons of biomass annually by the year 2022 (assuming current cellulosic and corn grain ethanol yields).[9] A 2005 report by the US Department of Energy and the US Department of Agriculture (DoE and USDA, respectively) estimated that the USA has the potential to displace up to 30% of its 2004 petroleum consumption, equivalent to 227 billion liters of ethanol on an energy-adjusted basis, with renewable ethanol.[9] This optimistic estimate is contingent on significant improvements across the entire feedstock production supply chain, such as feedstock yield improvements of 50%, dramatic land-use changes including the use of idle cropland for bioenergy crop production, 75% removal of crop residue, and universal adoption of reduced and/or conservation tillage practices, to name a few.[9] However, the sustainability of harvesting such large quantities of biomass, in terms of soil carbon balance, was not considered. For example, studies suggest that to maintain soil carbon levels, agricultural residues cannot be removed in large quantities, and in some instances cannot be removed at all.[10,11] Furthermore, the impact of expanding dedicated energy crop production to meet expected cellulosic ethanol demand could have negative global impacts if this expansion occurs on lands that are currently used for crop production or if high-carbon lands are converted to produce dedicated bioenergy crops.[12,13] In addition to conventional production of dedicated energy crops and collection of agricultural and forest residues, several synergistic production options have been suggested that utilize non-arable lands and/or degraded lands in conjunction with polycultures of native flora. Such strategies take advantage of lands that do not compete with current agricultural production as well as mixtures of legumes and forbs that reduce nutrient demand;[14,15] however, such options have not been part of a national-level resource assessment. At time of writing, DoE and USDA are updating their original biomass availability estimates.

Biomass-to-ethanol yield (volume of EtOH per mass of feedstock) at the biorefinery and delivered feedstock cost (which encompasses all feedstock production, harvest, and pre-processing steps) are two of the key parameters affecting both ethanol selling price and the overall sustainability of bioethanol production. Understanding how upstream processes – such as feedstock harvest and collection, handling, transport, storage – and pre-processing affect biochemical conversion will identify areas that offer opportunities to make the feedstock more compatible with conversion processes while decreasing supply cost. The objectives of this review are (i) to summarize the peer-reviewed literature with regard to the primary harvest-to-reactor throat variables that affect feedstock composition and conversion to ethanol; (ii) to identify current knowledge gaps; and (iii) to recommend steps needed to move the science forward. This review is focused on biochemical conversion (dilute-acid simultaneous saccarification and fermentation) of cellulosic biomass derived from both agricultural residues and dedicated energy crops. Logistics associated with other cellulosic conversion technologies, such as pyrolysis and gasification, will likely be very different than logistics associated with biochemical conversion, particularly with regard to the pre-processing steps needed. Discussion of the logistics needed for these technologies deserves their own treatment and is beyond the scope of this review.

Farm-to-reactor throat processes

From the time a biomass crop is ready for harvest to when it is eventually fed into a bioreactor, several unit processes occur (Figure 1). Regardless of whether a particular feedstock is a dedicated bioenergy crop or an agricultural or woody residue, it will be harvested, transported, queued and/or stored, and pre-processed before it can be fed into a bioreactor. The remainder of this review will focus on these key unit operations and their effects on biochemical conversion to ethanol, with emphasis on enzymatic hydrolysis as a conversion method.

Harvest timing

Harvest timing can have significant impacts on biomass yield, chemical composition and moisture content.

Biomass yield

Harvest strategies specific to bioenergy crops are evolving, yet there remains a limited number of studies that are specific to the harvest of cellulosic feedstocks. Although the basic goal of optimizing material collection and minimizing uncontrolled losses remains the same, such strategies are likely to differ from those for forage and/or commodity-type crops. Attributes that are desirable from a biochemical conversion standpoint are somewhat different than those from a livestock nutritional aspect. It is important for both biomass producers and biorefineries to balance the economics of harvest timing with biomass yield, harvest window, and optimal composition. Harvest management (e.g. harvest timing) has been shown to significantly affect biomass yields in switchgrass, with some cultivars of switchgrass attaining 50% greater yields when harvested twice per season compared with one harvest per season.[16,17] In contrast, other studies have shown that maximum switchgrass biomass yields are achieved with a single harvest during the R3 to R5 crop growth stage (mid-reproductive stage).[18]

These studies illustrate the regional differences in management required to maximize yields of the same species grown. McLauchlin *et al.* suggest that the yield differences observed among the harvesting strategies (one *vs* two

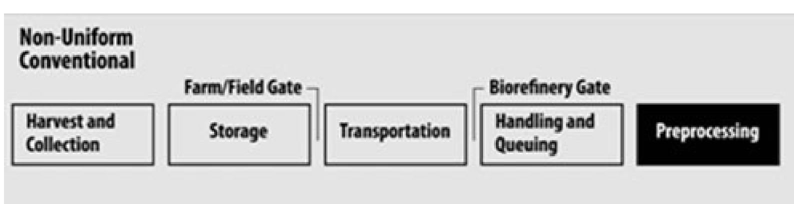


Figure 1. Conventional feedstock supply system designs consist of a series of unit processes which include harvest and collection, storage, transportation and handling, receiving and pre-processing. In the conventional supply system pre-processing occurs only at the depot located adjacent to the conversion facility. (Figure from Hess *et al*.[28] used with permission.)

harvests per season) are because of water availability differences.[17] The two-cut system produces higher overall yields in areas that are less climatically variable. In contrast, switchgrass grown in areas that have water availability issues will have the greatest yields with only one harvest per season. The authors attribute this to the two-harvest system impeding deep root development and thus access to soil water.[17] These results underscore the need to develop regionally specific management guidelines for feedstock producers. Furthermore, it is unclear whether these findings are applicable to other dedicated herbaceous bioenergy crops, such as miscanthus and mixed prairie grasses, as these questions are currently unanswered.

The time of year that biomass is harvested is important from both a logistical and a compositional perspective. Delaying harvest until after a killing frost (late fall/early winter) is common practice for many forage crops. Delaying harvest until spring, however, can have undesirable yield consequences. For example, spring-harvested miscanthus and switchgrass have been shown to have significant biomass yield losses compared with fall-harvested biomass.[19,20] The primary reason for the observed yield loss is over-winter lodging (i.e. the plant has fallen over), which is exacerbated by winter snow accumulation and/or rainfall. Biomass that has lodged cannot be collected using conventional cutting and baling equipment. Adler *et al.*[20] found that switchgrass harvested with standard harvesting equipment during the fall resulted in the collection of 79% of the total standing biomass; 21% was left on the field. In contrast, switchgrass harvested during the spring resulted in the collection of only 55% of the total standing biomass.[20]

Similarly, crop residues have been shown to have the highest biomass yields when co-harvested with the primary crop. In a study by Pordesimo *et al.* biomass yields for corn stover were shown to be greatest when harvested at the same time as the grain.[21] During grain harvest, the stover is damaged by the harvesting and transportation equipment, which exacerbates lodging and material loss. On the other hand, research suggests that although biomass yield may be lower for spring harvest, the nitrogen fertilizer input needed for the following growing season may also be lower because nitrogen relocates to the crowns following a killing frost. Being translocated to the crowns allows the nutrient to be used by the crop the following growing season, as opposed to being lost with the harvested material. This could be advantageous from many standpoints, including feedstock production economics and the overall sustainability of the feedstock production phase. Also, since spring harvest leaves more residues on the field compared with fall harvest, this could be part of a best management practice for situations when biomass needs to be left on the field to maintain soil carbon and moisture as well as to prevent erosion. A study that examines the life cycle economic and sustainability tradeoffs between fall and spring harvest could help to resolve this issue.

Chemical composition

In forage studies, harvest timing has been shown to significantly affect chemical composition and thus forage quality (i.e. ruminant digestibility, nutritive content). Because of seasonal and diurnal nutrient and chemical cycling within the plant, the time of year and the time of day of harvest have been shown to influence forage quality.[22] Both perennial and annual plants cycle nutrients and plant metabolites through their vascular tissues in response to temperature and photoperiod. For example, sorghum harvested during the vegetative crop growth stage (i.e. before flowering) has been shown to have improved livestock nutritive value compared with sorghum harvested at a later crop growth stage.[23] In a forage sorghum cropping trial, Prostko *et al.*[24] found that harvest timing had a significant effect on protein, acid detergent fiber (ADF), and neutral detergent fiber (NDF), with all components being lowest when the crop was harvested at the soft-dough crop growth stage (15–25 days after flowering[25]). The effect of harvest timing on forage nutritive content and digestibility is likely attributable, in part, to the rapid translocation of sugars, amino acids, and proteins from the plant vascular tissues to the kernels following the flowering stage.[25] Although harvest timing clearly influences characteristics that affect forage quality, strategies to maximize forage quality may not be applicable to maximizing ethanol feedstock quality.

Feedstock quality and composition is significantly affected by harvest timing because the location and concentration of sugars within the plant changes in response to environmental and physiological cues.[20] Crop maturity at the time of harvest affects the quantity of soluble sugars and the ease with which glucans are extracted from the substrate.[26] Dien[26] found that in general, the percent glucose recovery decreased significantly with increased crop growth stage for switchgrass, reed canary grass, and alfalfa under dilute-acid pre-treatment conditions. Although the cell wall glucose and non-glucose sugar concentrations increased with maturity, lignin also increased, which significantly inhibited the sugar recovery during pre-treatment.[20,26] In contrast, the non-glucose sugar recovery was not affected by maturity, but rather by its concentration in the plant tissue and the pre-treatment temperature. Pordesimo *et al.* found that corn stover fractional composition changed significantly following the flowering stage (R1 crop growth stage). Stover becomes less amenable to biochemical conversion after flowering because the lignin and xylan contents increase concurrent with decreasing soluble solids content (total glucan less structural glucan).[27] As plants mature, non-cell-wall carbohydrates are reduced relative to structural carbohydrates.[26] Reduced soluble carbohydrate concentration has implications on overall conversion because these soluble carbohydrates are directly fermentable without pre-treatment but at the same time are highly susceptible to degradation.[26] From these studies, it can be surmised that the feedstock composition most amenable to biochemical conversion occurs when the feedstock is harvested earlier (i.e. after the flowering stage) rather than later in the season. However, as we will discuss later, early harvest has other logistical issues that need to be balanced with optimal feedstock composition for conversion to biofuels.

Water content

In addition to affecting biomass chemical composition, harvest timing also has a direct influence on the water content of the harvested feedstock. The water content of the harvested feedstock can significantly affect transportation requirements, energy usage at the refinery (i.e. for feedstock drying and comminution), stability of the stored material, and available energy content (e.g. lower heating value (LHV)).[19,20] Although herbaceous feedstocks are often dried in a windrow to reduce moisture content prior to baling, some advanced harvesting and collection strategies are being developed that cut and collect the biomass in a single pass, increasing the harvest window and decreasing dry matter losses.[28] Harvest timing should be examined in the context of the entire ethanol supply chain (e.g. life cycle assessment) to develop a clear understanding of the tradeoffs and advantages of various harvest strategies in relation to biomass composition and quality.

Harvested components

The chemical composition of different plant components varies depending on the physiological function of each component. Determining which plant components are most efficiently converted to ethanol will likely become important, especially with regard to the collection and use of agricultural residues. Once thought of as a waste product, agricultural residues have been shown to have an important role in preventing soil erosion, maintaining soil moisture, and maintaining soil organic carbon,[10,11,29–31] in addition to providing feed and bedding for livestock.[32] Developing strategies that selectively harvest ‘high-value’ plant components for ethanol conversion, while leaving the rest on the field to decompose, may help balance energy needs with soil sustainability needs.

By weight, standing corn stover (excluding cob and grain) is composed of approximately 25% sheath, 36% blade, and 39% stem.[33] The brittle nature of the leaf makes it difficult to effectively harvest. Both sheath and blade proportions have been found to be much lower in baled stover than in stover that is standing in the field.[33] From a conversion perspective, this is problematic, because the stems contain higher amounts of lignin compared with the leaf components. The higher recalcitrance of the stems necessitates harsher pre-treatment prior to conversion.

Glucose production following enzymatic hydrolysis has been shown to vary significantly for different corn stover fractions;[34] after 60 hours, 300% more glucose was hydrolyzed from cobs, leaves, and husks than from stalks. Duguid *et al.* also found that composition, and therefore ethanol conversion yields, varied significantly among corn stover fractions.[35] While glucan content was similar across husks, leaves, cobs, and stems, increases in xylan with corresponding decreases in lignin were observed in husk and cob fractions compared with the content of the rest of the fractions.[35] Cob, leaf, and husk fractions responded better to both acid and alkaline pre-treatments than did stem and whole stover fractions. Higher yields of glucan were realized

  | *Biofuels, Bioprod. Bioref.* 4:562–573 (2010); DOI: 10.1002/bbb

under pre-treatment and enzymatic hydrolysis in non-stem corn stover fractions, and theoretical ethanol production followed these trends as well. The moisture content of stover fractions has also been shown to vary among components, with the stalks generally having higher moisture content than either the leaves or cobs.[21]

Similarly, wheat stover fractions showed variation in composition. Chaff fractions responded well to dilute-acid pre-treatment with an increase in glucan conversion from 16% to 82% following pre-treatment;[36] interestingly, the native leaf fraction (not dilute acid pre-treated) resulted in a theoretical ethanol yield of greater than 76%, which is not significantly different from the ethanol yield of pre-treated leaves.

Switchgrass plant components have also been shown to differ compositionally. Griffin and Jung[37] showed that switchgrass stems and leaves differed significantly on the basis of lignin, NDF, crude protein, and *in vitro* dry matter disappearance. Furthermore, they found that the proportion of leaf/stem decreased significantly following seed-head emergence and that the lignin content of the stem increased with maturity. Selectively collecting desirable plant components (e.g. leaves) while leaving more recalcitrant material on the field could lead to more sustainable practices both in the field, by returning carbon and nutrients to the soil, and at the biorefinery, by requiring less severe pre-treatment conditions.

Biomass storage

Biomass storage is a key element in the biomass supply chain for maintaining a year-round feedstock supply to a refinery. Storage infrastructure will vary depending on the feedstock quantity and quality needs of the refinery as well as the conversion technology, climate, space available for storage, feedstock format (i.e. bales *vs* pellets), and the type of feedstock. There is a long history of biomass storage research and industrial experience from the forage, pulp and paper, and agricultural grains industries that offers insights into the relative advantages and disadvantages of several storage options.

Given the short harvest window for biomass, while biorefineries are continuous year-round operations, the need to provide aerobically stable feedstock is critical to meeting the demands of a cellulosic biofuels industry. Feedstock moisture affects all elements of the supply chain, and a large portion of the US biomass available to support a renewable fuels industry will be wet (i.e. >25 w% moisture) at the time of harvest.[28] Biomass is considered dry when it is harvested at or below 20–25% moisture;[38] however, the moisture content of corn stover at grain harvest reportedly ranges from 20 to 65 w%.[39,40] Wet biomass poses two major problems in terms of the increased cost associated with the transport of wet material and the inherent instability of wet material, which makes it prone to microbial degradation and subsequent dry matter loss. Drying methods are often employed to mitigate the negative impacts of unstable wet material on the supply chain. A common mitigation method is field drying prior to baling, which can significantly reduce the moisture content of the biomass. However, the extent to which field drying is effective depends on the region and the local weather conditions during the harvest season. If the biomass is collected while wet, as would be in the case when using a single-pass harvester,[28] mechanical dryers may be required prior to conversion. However, the process of drying is energy intensive, may increase biomass recalcitrance,[41,42] and comes at a significant cost to the supply chain. For example, the US Corn Belt leads the nation in expenditure on propane, which is used extensively for crop drying.[43]

On-field storage of biomass has been used as a primary means of storing forage for centuries and has advantages from both an economic and a logistical standpoint. Many biomass feedstocks and common forage crops can be handled and stored similarly (e.g. can be harvested and baled using standard haying equipment); indeed, many forage crops can be used as ethanol feedstocks. However, the biofuels supply chain is unlike the forage industry in that there is a need for a consistent and constant supply of large volumes of biomass to a specific location(s). Although convenient, baling and storing biomass on the field or in another uncovered area has the potential to significantly reduce both the quantity and the quality of the stored biomass and thus negatively affect the efficiency of the entire feedstock-to-ethanol system.[44] Switchgrass harvested and stored as round bales has been shown to lose significant amounts of ethanol-extractable components when stored outside and exposed to weather events.[45] Wiselogel *et al.* showed that switchgrass round bales can lose as much as 11 w% of the ethanol extractable components, depending on the degree of weathering. Outdoor bale storage on a concrete pad versus storage inside a barn resulted in a 4–8% reduction of hydrolyzable glucose in whole corn stover after nearly eight months of storage.[34] Corn stover bales stored outside for up to eight months have been shown to have dry matter losses of as much as 18%, whereas corn stover stored for an equivalent amount of time in a covered area lost only 3% of the dry matter.[38]

Shinners found that ensiled corn stover dry matter losses were statistically equivalent to the dry matter losses observed for corn stover bales stored indoors. Ensiling is a traditional method for crop preservation that has been in use for centuries, and which is still used in modern agricultural practice;[46] this process relies on the microbial conversion of soluble sugars in fresh plant material to organic acids (e.g. lactic and acetic acids). The combination of low pH and anaerobic conditions that results from the ensiling process precludes the growth of detrimental fungi and bacteria, allowing for the preservation of dry matter. Ensiling is advantageous for biochemical conversion because it does not require field-drying, which expands the harvest window,[41] resulting in greater yields (i.e. the feedstock can be harvested earlier in the season), and more uniform product.[38] Another advantage of ensiled material over baled material is that it does not necessitate a permanent storage facility if plastic ensiling wrap is used. Ensiling has also been shown in some studies[47,48] to improve the biochemical conversion of cellulosic biomass to ethanol. It has been suggested that the acidic environment of ensiled materials aids in the solubilization of hemicellulose.[47–49] In a study of the effect of ensiling across several cellulosic feedstocks (barley straw, triticale straw, wheat straw, cotton stalks, and triticale hay), Chen found that ensiling does improve the hydrolysis of cellulosic biomass compared with hydrolyzing untreated biomass, but ensiling alone is not as effective as chemical pre-treatment strategies. A recent study by Thomsen[50] reported nearly 100% glucose recovery and 80% xylose recovery following hot water pre-treatment of whole crop maize silage (stem, leaves, and grain); however, glucan recoveries following pre-treatment were likely high in this study due to the increased starch content of whole crop material relative to typical lignocellulosic feedstocks. The ethanol yield achieved for whole maize silage after low severity hot water pre-treatment (185 °C, 15 min) was 98% of theoretical. These findings demonstrate the potential for silage to serve as a promising material for biofuel production. More work is needed to examine the required energy inputs as well as to determine how ensiling affects conversion of different feedstocks. Although the water content of ensiled material is greater than with other storage options, a 2007 modeling study found that the delivered costs of ensiled switchgrass are competitive with baled switchgrass on a dry basis (\$44–\$47 dry ton^{-1} for round bales versus \$48 dry ton^{-1} for ensiled material).[51]

Both wet and dry biomass storage options have been explored by researchers in the pulp and paper industry since the early twentieth century.[52–54] Disadvantages of dry storage, such as fire danger, prompted the pulp and paper industry to adopt wet storage (75–85 w% moisture) as the industry standard during the mid-twentieth century.[55] In addition to reducing fire danger, wet-stored biomass has been shown to remain compositionally stable for long periods of time.[55] Several studies report that wet-stored bagasse is superior to fresh bagasse for paper making because the stored material has both higher holocellulose and pentosan concentrations and lower soluble concentrations,[55] and that a reduction in the pulping requirements without affecting paper quality is observed compared with fresh baggase requirements. But as mentioned earlier, from a biochemical conversion perspective it is plausible that the necessary drying could be prohibitively costly unless the biomass was wet-stored at or very near the biorefinery.

Pre-processing

Biomass pre-processing (i.e. preparing the material for transport, storage, and feeding into the reactor) is integral to an efficient feedstock supply chain. Pre-processing is needed to improve material stability, improve flowability of the biomass material, and increase bulk density, all of which decrease handling and distribution costs.[28] Transport of unprocessed biomass can result in as much as 15% material loss because of multiple handling operations; densified biomass has much less material loss during transport.[56] Pre-processing decreases the particle size of the material, increasing the surface area, which could make cellulosic material more amenable to pre-treatment processes and enzymatic hydrolysis.[57] Based on the Idaho National Laboratory's (INL's) recent feedstock logistics design report,[28] the location of the pre-processing operation is envisaged to change as the cellulosic ethanol industry

  | *Biofuels, Bioprod. Bioref.* **4**:562–573 (2010); DOI: 10.1002/bbb

expands to meet projected ethanol demand. According to its report and supporting techno-economic analysis, the conventional bale-based system cannot meet national-level biofuel cost targets (e.g. being cost-competitive with conventional gasoline) such as those mandated in the 2007 RFS,[8,28] nor can it supply the quantity of biomass necessary to meet these goals because the delivered feedstock costs are projected to be too high. Therefore, the INL study proposes moving the pre-processing operation to as early in the supply chain as is practical, and away from the biorefinery (Figure 2). These localized pre-processing depots would greatly improve upstream efficiency and increase material stability, which decreases losses, and would be conducive to blending different quality feedstocks to meet the specifications of different conversion processes. The pre-processing depots allow for a more flexible biofuels system because the biorefineries would not be constrained to local feedstock resources and could accept a much broader ranges of feedstocks. The ability to diversify feedstocks also supports crop rotations, which promote soil health. Moving beyond local resources allows refineries to take advantage of capital economies of scale, which would decrease production costs and relieve the refinery's vulnerability to local supply conditions. Additionally, a uniform format feedstock supply can be handled in existing high-capacity, proven, and efficient systems, such as those used in the grain (for a bulk solid format) or petroleum (for a bulk liquid format) industries, which could improve plant efficiency. Benefits of a uniform format system go further, allowing for a commodity-based biomass system analogous to the current grain industry, which incorporates small resources that are presently stranded and creates a consistent pricing system.[28] However, all of these benefits rely on a step change from the conventional supply systems to a depot-style supply system.

Particle size reduction

The particle size reduction required as part of the pre-processing operation provides the opportunity for fractionation of the biomass into multiple size fractions with variable conversion efficiencies. Chundawat *et al.* found that milled corn stover fractions had markedly different compositional makeup across the range of size fractions analyzed. Larger particle size fractions were found to have higher levels of xylan and mannan compared with the smaller size fractions; therefore, the larger size fractions have more hemicellulose than their smaller counterparts.[58] Conversely, the smaller size fractions had higher levels of water- and alcohol-soluble compounds. The authors attribute these differences in compositional make-up to the preferential nature of specific plant components to aggregate into different size fractions upon grinding. For example, the authors speculate that the leaves tend to be processed into the finest fractions, while the more resistant materials such as the stems tend to separate into larger-size fractions.[58]

Particle size and size fractionation have significant effects on the pre-treatment and conversion processes. As mentioned previously, particle size reduction increases the surface area of the substrate, which can lead to improved enzymatic hydrolysis under certain conditions.[59] However, increased surface area is not optimal for all feedstock and pre-treatment processes. Reduced particle size has been shown to improve enzymatic hydrolysis of corn stover pretreated using ammonia fiber explosion (AFEX), but to be deleterious to the conversion of steam-explosion-treated wood chips.[60] Other studies indicate that particle sizes

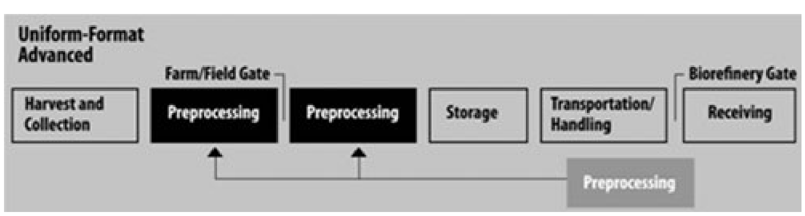


Figure 2. Advanced uniform-format feedstock supply system designs adapt lignocellulosic biomass to current high-efficiency logistics systems by preprocessing the biomass into a high-density/aerobically stable material at or near the point of the resource origination. (Figure from Hess *et al*.[28] used with permission.)

below a certain level (40-mesh; ≤420 μm) have no effect on biomass digestibility and conversion.[61–63] Although the production of pellets is energy intensive, pelletizing biomass feedstocks is one potential means of pre-processing biomass into a high bulk density, aerobically stable, flowable material. Pellets, flour, granules, and biocrude are all densified, uniform formats being considered by the INL[28] to meet the nation's long-term biofuels production cost and quantity goals. Although several studies have examined the chemical composition and biochemical conversion efficiencies of the different size fractions that result from grinding/milling cellulosic biomass, there is a dearth of information on the effect that biomass pelletization has on the pre-treatment and conversion processes. All components of the supply system need to be optimized together to minimize system cost. For example, ensiling may be an advantageous storage option for some conversion platforms that use a wet material; however, transportation and handling costs are higher. Alternatively, pelletizing requires significant energy resources for drying and pellet formation, but the resulting format is cheaper to handle and transport and is a more suitable feedstock for processes that require a dry material.

Conclusions

After review of the literature, it is salient that more research is needed to establish clear harvest, pre-processing, and storage strategies that are specific to feedstocks for ethanol production. Literature indicates that fall-harvested biomass generally results in higher yields, but spring-harvested biomass may have advantages in terms of sustainability. Further study is needed to quantify the relative advantages of specific harvest strategies over the entire life cycle of cellulosic ethanol. Much of the literature on harvest strategies and chemical composition of biomass is from forage studies, which rely on indicators of forage quality (e.g. NDF, ADF, protein) as a basis for analysis. More work should be performed that focuses on the chemical constituents that are important from a biochemical conversion perspective. Storage research specific to ethanol feedstocks is also lacking. Studies indicate that storing biomass outside and uncovered results in both material loss and loss of feedstock quality. Some studies suggest that ensiling or other wet-storage options have benefits such as improved chemical stability and less storage space. However, none of the studies address the additional energy inputs that would be needed to transport and dry the wet biomass.

Significant research gaps exist in the areas of harvest timing, storage strategies, and biomass pre-processing. These unit processes have significant effects on biomass yield, material loss, energy consumption, system cost, and chemical composition. Improved understanding is needed in these areas to optimize the feedstock supply chain and to facilitate large-scale deployment of biomass-based liquid transportation fuels in the USA and abroad.

Pre-processing biomass into a more easily transported and handled material is needed to facilitate large-scale deployment of biomass-based liquid transportation fuels. Additionally, a network of pre-processing depots would provide opportunities to increase feedstock quality and enhance supply system logistics costs. However, in the peer-reviewed literature there is a dearth of comparative studies that examine multiple pre-processing options.

The effect of different pre-treatment strategies on composition and conversion efficiency is well understood but continues to evolve. Work continues to bring pre-treatment technologies from bench and pilot scales to demonstration and commercial scales; increased solids loadings and higher throughput methodologies are currently receiving much attention. As many regulatory agencies throughout the world move toward holistic assessment of biofuels using life cycle assessment tools, there is a real need to examine key processing steps from a life cycle perspective.

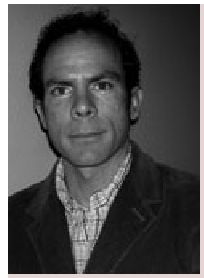
References

1. Kerr RA, The looming oil crisis could arrive uncomfortably soon. *Science* **316**:351 (2007).
2. Kerr RA, Global warming is changing the world. *Science* **316**:188–190 (2007).
3. Licht FO, World Ethanol Report. Agra Informa Ltd, Kent, UK (2008).
4. EIA. Petroleum Basic Statistics. Washington, DC (2009). Available at: http://www.eia.doe.gov/basics/quickoil.html [July 27, 2009].
5. EPA. Inventory of US Greenhouse Gas Emissions and Sinks: 1990–2007. US Environmental Protection Agency, Washington, DC, EPA 430-R-09-004 (2009).
6. EIA. Greenhouse gases, climate change and energy. US Department of Energy, Energy Information Administration, Washington, DC, DOE/EIA-X012 (2008).
7. CARB. The California Low Carbon Fuel Standard Regulation – Draft. California Air Resources Board, Sacramento, CA (2008).
8. EISA. Energy Independence and Security Act of 2007. Public Law 110–140 (2007).

  | *Biofuels, Bioprod. Bioref.* **4**:562–573 (2010); DOI: 10.1002/bbb

9. Perlack RD, Wright LL, Turhollow AF, Graham RL, Stokes BJ and Erbach DC, Biomass as feedstock for a bioenergy and bioproducts industry: The technical feasibility of a billion-ton annual supply. United States Department of Energy, Oak Ridge National Laboratory, Oak Ridge, TN, DOE/GO-102005-2135, ORNL/TM-2005/66 (2005).
10. Wilhelm WW, Johnson JM-F, Karlen DL and Lightle DV, Corn stover to sustain soil organic carbon further constrains biomass supply. *Agron J* **99**:1664–1667 (2007).
11. Johnson JMF, Allmaras RR and Reicosky DC, Estimating source carbon from crop residues, roots and rhizodeposits using the national grain-yield database. *Am Soc Agron* **98**:622–636 (2006).
12. Searchinger T, Heimlich R, Houghton RA, Dong F, Elobeid A, Fabiosa J *et al.,* Use of US croplands for biofuels increases greenhouse gases through emissions from land-use change. *Science* **319/5867**:1238–1240 (2008).
13. Fargione J, Hill J, Tilman D, Polasky S and Hawthorne P, Land clearing and biofuel carbon debt. *Science* **319/5867**:1235–1238 (2008).
14. Tilman D, Hill J and Lehman C, Carbon-negative biofuels from low-input high-diversity grassland biomass. *Science* **314**:1598–1600 (2006).
15. Tilman D, Socolow R, Foley JA, Hill J, Larson ED, Lynd LR *et al.,* Beneficial biofuels – The food, energy, and environment trilemma. *Science* **325**:270–271 (2009).
16. Reed RL, Sanderson MA, Hussey MA, Ocumpaugh WR, Reed JC, Tischler LR *et al.,* Biomass production and allocation of switchgrass cultivars in Texas. Texas A&M University, College Station, TX (1994).
17. McLaughlin S, Bouton J, Bransby D, Conger B, Ocumpaugh W, Parrish D *et al.,* Developing switchgrass as a bioenergy crop, in *Perspectives on New Crops and New Uses*, ed by Janick J. ASHS Press, Alexandria, VA, pp. 282–99 (1999).
18. Vogel KP, Brejda JJ, Walters DT and Buxton DR, Switchgrass biomass production in the Midwest USA: Harvest and nitrogen management. *Agron J* **94**:413–420 (2002).
19. Lewandowski I, Clifton-Brown JC, Andersson B, Basch G, Christian DG, Jørgensen U *et al.,* Environment and harvest time affects the combustion qualities of miscanthus genotypes. *Agron J* **95**:1274–1280 (2003).
20. Adler PR, Sanderson MA, Boateng AA, Weimer PJ and Jung H-JG, Biomass yield and biofuel quality of switchgrass harvested in fall or spring. *Agron J* **98**:1518–1525 (2006).
21. Pordesimo LO, Sokhansanj S and Edens WC, Moisture and yield of corn stover fractions before and after grain maturity *Trans ASABE* **47/5**:1597–1603 (2004).
22. Huntington GB and Burns JC, Afternoon harvest increases readily fermentable carbohydrate concentration and voluntary intake of gamagrass and switchgrass baleage by beef steers. *J Anim Sci* **85**:276–284 (2007).
23. McCormick ME, Morris DR, Ackerson B and Blouin DC, Ratoon cropping forage sorghum for silage : yield, fermentation, and nutrition. *Agron J* **87**:951–957 (1995).
24. Prostko EP, Muir JP and Stokes SR, The influence of harvest timing on forage sorghum silage quality and yield. Texas A&M University, College Station, TX (1998).
25. Gerik T, Bean B and Vanderlip R. Sorghum growth and development. Texas A&M University, College Station, TX (2003).
26. Dien BS, Jung H-JG, Vogel KP, Casler MD, Lamb JFS, Iten L *et al.,* Chemical composition and response to dilute-acid pretreatment and enzymatic saccharification of alfalfa, reed canarygrass, and switchgrass. *Biomass Bioenerg* **30**:880–891 (2006).
27. Pordesimo LO, Hames BR, Sokhansanj S and Edens WC, Variation in corn stover composition and energy content with crop maturity. *Biomass Bioenerg* **28**:366–374 (2005).
28. Hess JR, Kenney KL, Park L, Searcy EM and Wright CT, Uniform-format solid feedstock supply Ssystem: A commodity-scale design to produce an infrastructure-compatible bulk solid from lignocellulosic biomass. Idaho National Laboratory, Idaho Falls, ID, INL/EXT-08-14752 (2009).
29. Lindstrom MJ, Skidmore EL, Gupta SC and Onstad CA, Soil conservation limitations on removal of crop residues for energy production. *J Environ Qual* **8**:533–537 (1979).
30. Sheehan J, Aden A and Riley C. Corn stover life cycle analysis. National Renewable Energy Laboratory, Golden, CO (2000).
31. Graham RL, Nelson R, Sheehan J, Perlack RD and Wright LL, Current and potential US corn stover supplies. *Agron J* **99**:1–11 (2007).
32. Fernandez-Rivera S and Klopfenstein TJ, Yield and quality components of corn crop residues and utilization of these residues by grazing cattle. *J Anim Sci* **8**:597–605 (1989).
33. Akin DE, Morrison WH, III, Rigsby LL, Barton FE, II, Himmelsbach DS and Hicks KB, Corn stover fractions and bioenergy. *Appl Biochem Biotechnol* **129–132**:104–116 (2006).
34. Montross MD and Crofcheck CL, Effect of stover fraction and storage method on glucose production during enzymatic hydrolysis. *Bioresour Technol* **92**:269–274 (2004).
35. Duguid KB, Montross MD, Radtke CW, Crofcheck CL, Wendt LM and Shearer SA, Effect of anatomical fractionation on the enzymatic hydrolysis of acid and alkaline pretreated corn stover. *Bioresour Technol* **100**:5189–5195 (2009).
36. Duguid KB, Montross MD, Radtke CW, Crofcheck CL, Shearer SA and Hoskinson RL, Screening for sugar and ethanol processing characteristics from anatomical fractions of wheat stover. *Biomass Bioenerg* **31**:585–592 (2007).
37. Griffin JL and Jung GA, Leaf and stem forage quality of big bluestem and switchgrass. *Agron J* **75**:723–726 (1983).
38. Shinners KJ, Binversie BN, Muck RE and Weimer PJ, Comparison of wet and dry corn stover harvest and storage. *Biomass Bioenerg* **31**:211–221 (2007).
39. Shinners KJ, Binversie BN and Savoie P, Whole–plant corn harvesting for biomass: Comparison of single-pass and multiple-pass harvest systems. 2003 ASAE Annual International Meeting, July 27– 30 Riviera Hotel and Convention Center, Las Vegas, Nevada, USA (2003).
40. Hoskinson RL, Karlen DL, Birrell SJ, Radtke CW and Wilhelm WW, Engineering, nutrient removal, and feedstock conversion evaluations of four corn stover harvest scenarios. *Biomass Bioenerg* **31**:126–136 (2007).
41. Esteghlalian AR, Bilodeau M, Mansfeld SD and Saddler JN, Do enzymatic hydrolyzability and simons' stain reflect the changes in the accessibility of lignocellulosic substrates to cellulase enzymes? *Biotechnol Prog* **17**:1049–1054 (2001).
42. Jeoh T, Ishizawa CI, Davis MF, Himmel ME, Adney WS and Johnson DK, Cellulase digestibility of pretreated biomass is limited by cellulose accessibility. *Biotechnol Bioeng* **98**:112–122 (2007).

43. Schnepf R, *Energy use in agriculture: Background and issues.* Congressional Research Service, Washington, DC (2004).
44. Rentizelas AA, Tolis AJ and Tatsiopoulos IP, Logistics issues of biomass: The storage problem and the multi-biomass supply chain. *Renew Sust Energ Rev* **13**:887–894 (2009).
45. Wiselogel AE, Agblevor FA, Johnson DK, Deutch S, Fennell JA and Sanderson MA, Compositional changes during storage of large round switchgrass bales. *Bioresour Technol* **56**:103–109 (1996).
46. McDonald P, Henderson AR and Heron SJE, *The Biochemistry of Silage, 2nd Edition*. Chalcombe Publications, Marlow, Bucks, UK (1991).
47. Chen Y, Sharma-Shivappa RR and Chen C, Ensiling agricultural residues for bioethanol production. *Appl Biochem Biotechnol* **143**:80–92 (2007).
48. Singh K, Honig H, Wermke M and Zimmer E, Fermentation pattern and changes in cell wall constituents of straw-forage silages, straws and partners during storage. *Animal Feed Sci Technol* **61**:137–153 (1996).
49. Linden JC, Henk LL, Murphy VG, Smith DH Gabrielsen BC, Tengerdy RP *et al.,* Preservation of potential fermentables in sweet sorghum by ensiling. *Biotechnol Bioeng* **30**:860–867 (1987).
50. Thomsen MH, Holm-Nielsen JB, Oleskowicz-Popiel P and Thomsen AB, Pretreatment of whole-crop harvested, ensiled maize for ethanol production. *Appl Biochem Biotechnol* **148**:23–33 (2008).
51. Kumar A and Sokhansanj S, Switchgrass (Panicum vigratum, L.) delivery to a biorefinery using integrated biomass supply analysis and logistics (IBSAL) model. *Appl Biochem Biotechnol* **98**:1033–1044 (2007).
52. Lathrop EC and Munroe TB, *Methods of Preserving Fiber for Pulp-Making Purposes*. US Patent 1,572,540 (1926).
53. Munroe TB and Lathrop EC, *Fiber Storage and Preservation*. US Patent 1,920,129 (1933).
54. Hay HR and Lathrop EC. Storage of crop fibers and preservation of their properties. TAPPI Technical Association Papers, pp. 412–418 (1941).
55. Atchison JE and Hettenhaus JR, Innovative methods for corn stover collecting, handling, storing and transporting. National Renewable Energy Laboratory, Golden, CO (2004).
56. Hamelinck CN, Suurs RAA and Faaij APC, International bioenergy transport costs and energy balance. *Biomass Bioenerg* **29**:114–134 (2005).
57. Gharpuray MM, Lee Y and Fan LT, Structural modification of lignocellulosics by pretreatments to enhance enzymatic hydrolysis. *Biotechnol Bioeng* **25**:157–172 (1983).
58. Chundawat SPS, Venkatesh B and Dale BE, Effect of particle size based separation of milled corn stover on AFEX pretreatment and enzymatic digestibility. *Biotechnol Bioeng* **96**:219–231 (2006).
59. Mansfield SD, Mooney C and Saddler JN, Substrate and enzyme characteristics that limit cellulose hydrolysis. *Biotechnol Progress* **15**:804–816 (1999).
60. Cullis IF, Saddler JN and Mansfield SD, Effect of initial moisture content and chip size on the bioconversion efficiency of softwood lignocellulosics. *Biotechnol Bioeng* **85**:413–421 (2004).
61. Chang VS and Holtzapple MT, Fundamental factors affecting biomass enzymatic reactivity. *Appl Biochem Biotechnol* **84–86**:5–37 (2000).
62. Chang VS, Burr B and Holtzapple MT, Lime pretreatment of switchgrass. *Appl Biochem Biotechnol* **63–65**:3–19 (1997).
63. Chang VS, Nagwani M and Holtzapple MT, Lime pretreatment of crop residues bagasse and wheat straw. *Appl Biochem Biotechnol* **74**:135–159 (1998).



Dr Daniel Inman

Danny joined NREL in February 2008. His research interests include sustainability of feedstock production, impacts of feedstock production on composition and conversion, land-use change impacts related to ethanol production, and improved management practices for energy crop production. He is currently working as part of a multidisciplinary team on a life cycle assessment of the ethanol mandates associated with the Energy and Independence and Security Act of 2007 where he is primarily responsible for modeling feedstock production systems. He also works with the Department of Energy's Office of the Biomass Program on several sustainability-related projects including quantifying direct and indirect land-use change using dynamic modeling and optimizing the sustainability of the biochemical conversion process.

Nick Nagle

Nick has worked on a number of projects from biodiesel production in microalgae to high solids anaerobic digestion. Since 1996, he has worked with the pre-treatment team on the installation and shakedown of pilot-scale pre-treatment reactors for biomass fractionation. He has project management experience on biomass conversion projects ranging from biodiesel production to waste management and expertise in microbiology, large-scale fermentation, and thermochemical pre-treatment of biomass, plus pilot- and engineering-scale experience with anaerobic digestion processes.

Jacob J. Jacobson

Jacob is a principal investigator for the Idaho National Laboratory. His fields of expertise include systems analysis and advanced modeling and simulation. His work has been in the development and analysis of decision support systems to evaluate policy options and business risks of complex energy and environmental systems. Applications include evaluation of long term stewardship issues, impacts from pollution on aquifers, future land use planning scenarios, nuclear fuel cycle analysis, and development of energy and greenhouse gas emission inventory and evaluation of carbon mitigation alternatives.

  | *Biofuels, Bioprod. Bioref.* **4**:562–573 (2010); DOI: 10.1002/bbb

Dr Erin Searcy

Erin is an engineer and analyst in the Biofuels and Renewable Energy Technologies Department at the Idaho National Laboratory. She specializes in the techno-economic analysis and modeling of biomass-based energy systems, particularly woody biomass and has also work as an engineering consultant, where she performed environmental impact assessments, designed water quality sampling programs, among other tasks.

Dr Allison E. Ray

Allison is a staff scientist in the Biofuels and Renewable Energy Technologies group at the Idaho National Laboratory. Her research interests include optimization of storage for preservation of feedstock quality and bioremediation of metals in subsurface environments. She holds a PhD in Environmental Microbiology and MSc and BSc degrees in Agricultural and Biological Engineering.